"SYNTHESIS AND CHARACTERIZATION OF PMMA BASED POLYMER GEL ELECTROLYTE"

Thesis Submitted for the Award of the Degree of

Master of Science

By

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DECLARATION

I hereby declare that the work carried out in this thesis is entirely original. It was carried out by me along with Miss Priyadarsini Padhi at Department of Physics, National Institute of Technology, Rourkela. I further declare that to the best of my knowledge the carried out experimental work has not formed the basis for the award of any degree, diploma, or similar title of any university or institution.

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CERTIFICATE

This is to certify that the thesis entitled "SYNTHESIS AND CHARACTERIZATION OF PMMA BASED POLYMER GEL ELECTROLYTE" being submitted by **Ranjeeta Giri** in partial fulfilment of the requirements for the award of the degree of Master of Science in Physics at National Institute of Technology, Rourkela is an authentic experimental work carried out by her under our supervision. To the best of our knowledge, the experimental matter embodied in the thesis has not been submitted to any other University/Institute for the award of any degree or diploma.

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My hearty gratitude to my parents, without them I cannot do anything.

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CONTENTS

ABSTRACT

A series of PMMA (poly(methyl methacrylate)) and NaI based polymer gel electrolytes were prepared with different concentration of O/Na ratio. Here we have chosen the values of O/Na ratio as O/Na=20, 40, 60, 80 and 100. For the preparation of the samples, we have taken poly(methyl methacrylate)as polymer, Ethylene carbonate + Propylene carbonate as solvent and Sodium iodide as salt. Free standing films of polymer gel electrolytes were prepared using gelation method. Samples were characterized by different experimental technique such as XRD, Optical microscopy, FTIR spectroscopy and Complex impedance spectroscopy. For structural properties of the material, X-ray diffraction technique is used. Optical microscopy is carried out to know the morphological properties. FTIR spectroscopy is carried out to observe the changes in the FTIR band present for different composition of O/Na. Dielectric Spectroscopy is carried out to analyse the dielectric and electrical behaviour of polymer gel electrolyte.

CHAPTER-1

INTRODUCTION

1.1 Electrolytes

When a salt is dissolved in a polar solvent like water, it get dissociates into its constituent ions giving rise to electrically conductive medium known as electrolyte [**1**]. Electrolytes are used in various electrochemical and electronic devices such as batteries, fuel cells, super capacitor, solar panel etc.

Electrolytes are of two types, depending upon their states: (1) Liquid electrolytes, (2) solid electrolytes [**1**].

1.2 Liquid electrolytes

When a salt dissolves in a solvent (which can be water or polar solvent), liquid electrolyte is formed i.e. NaCl dissolves in H_2O to form liquid electrolyte. The most appreciable property of liquid electrolyte is its high ionic conductivity, which is of the order of 10^{-2}S cm^{-1}**[2]** although liquid electrolyte is used in various electrochemical devices; still there are some shortcomings in liquid electrolyte. Those are

(i) they cannot be operated at a wide range of temperature
(ii) low power and energy density
(iii) failure of device because of corrosion of the electrodes by electrolytic solution
(iv) It is bulky in size and larger weight of the device due to the use of liquid electrolytes.

Liquid electrolytes also tend to leak out of the cells into which they are sealed **[2]**. So for these disadvantages, scientific community is leaning towards solid electrolytes.

1.3 Solid electrolytes

Solid which exhibits high ionic conductivity are known as solid electrolytes. The principal charge carriers are usually ions such as Li^+, H^+, Na^+, K^+, Ag^+, Ti^+, F^+, O^{2-}. Crystalline solids have high ionic conductivity due to: (1) high concentration of mobile ions, (2) low activation energy (E_a< 0.3 e V) for ionic motion from site to site, ionic interaction **[3]**.

1.4Classification of solid electrolytes:

There are different types of solid electrolytes [**4**]:

- Framework crystalline materials
- Amorphous glass electrolytes
- Polymer electrolytes
- Composites electrolytes

Framework crystalline materials

There are two types of framework crystalline materials.

(1) Soft framework crystalline materials
(2) Hard framework crystalline materials

Soft framework crystalline materials

In soft framework crystalline material, crystal bonding is mostly ionic. The mobile ions have very low melting point and also low Debye temperature. Therefore conduction is due to ion hopping and liquid like diffusion. The mobile ions are highly polarizable and heavy. Examples of soft framework crystalline material are AgI, CuI [**5**].

Hard framework crystalline materials

In hard framework crystalline material, crystal bonding is mostly covalent. The mobile ions have very high melting point, high Debye temperature and low polarizability. In this material conductivity is due to hopping of the mobile ions through the favourable sites of the material [**5**]. Hard framework crystals are generally oxides. It is most extensively studied both in single and polycrystalline form. Polycrystalline materials are mostly used in technological applications simply because they are easy to prepare and preparation cost is less [**5**].

Amorphous glass electrolytes

These electrolytes are ion conducting glass and they have different advantages over crystalline electrolytes. They have high ionic conductivity and also variable composition. In amorphous glass electrolytes the grain boundaries are absent and also used to fabricate in the form of thin film [**5**].

1.5 Polymer electrolytes

Polymer electrolytes are generally formed by complexation of high molecular weight polar polymers like Polyethylene oxide(PEO), Polypropylene oxide(PPO), Polyethylene glycol(PEG) etc. with ionic salts with low lattice energy and bulky anions. These ionic salts are of monovalent alkali metal or divalent transition metal [**5, 6**]. We can get rid of problems like (i) leakage of electrolyte, (ii) internal shorting, (iii) combustible reaction using solid electrolyte instead of liquid electrolyte. Solid polymer electrolytes have several advantages over its counterpart such as light weight, easy processability, good flexibility and elasticity. They also possess desired electrochemical stability and mechanical strength suitable for device applications [**2**].

There are mainly three different types of polymer electrolytes.

(i) Dry (solid) polymer electrolytes
(ii) Polymer composites electrolytes
(iii) Polymer gel electrolytes

(i) Dry (solid) polymer electrolytes

Solid polymer electrolyte better known as polymer salt complex is the first studied polymer electrolyte. This is formed by complexation of polymer with salt. Here the polymer host is used as solid solvent because the system does not possess any organic liquid. This system showed very low ambient temperature conductivities which is the order of 10^{-8} S cm^{-1}.Due to this poor ionic conductivity, this cannot be used in electrochemical devices [**2**].

(ii) Composite polymer electrolytes

These polymer electrolytes are also known as "composite ceramic electrolytes". High surface area fillers like ZrO_2, TiO_2, Al_2O_3 and hydrophobic fumed silica are usually incorporated into the solid polymer electrolytes known as composite polymer electrolytes [**2**]. There are two different advantages of incorporating the fillers: (1) Enhancement in ionic conductivity at ambient temperature (2) the second one is to improve the stability properties (i.e., thermal, electrochemical and mechanical).

(iii) Polymer gel electrolytes

Polymer gel electrolytes contains three terms: polymer, gel and electrolyte. To achieving higher and more practical ionic conductivity gel electrolytes are the alternative to the solvent free system. Gel possesses both the diffusive properties of liquid and cohesive properties of solid. These are formed by dissolving the salt in a polar liquid and adding polymer in it to give the material mechanical stability. The polymer gel electrolytes are flexible solid electrolytes and they are used in various devices such as rechargeable lithium batteries, sensors and display devices etc. The polymer gel electrolytes consists of three components; salt, solvent and polymer. The salt used must have low lattice energy and it provides ions for conduction. The solvent helps in dissolution of the ionic salt because it has a high dielectric constant. It also provides the medium for conduction and generally it has the active oxygen which helps in the formation of the co-ordination bond. Due to high molecular weight of the polymer, it provides mechanical strength and flexibility. Polymer gel electrolytes are used very wide range because of high conductivity [**6-8**]. Although polymer gel electrolytes possess desired level of ionic conductivity, still the electrochemical, mechanical and thermal stabilities are not suitable for device applications.

1.6 Literature survey

A.M. Voice *et.al.* prepared different series of thermoreversible gel electrolytes from various polymers and solvents by gel casting method. They have used lithium trifluoromethanesulfonate as the salt where Li-ion is the ionic species responsible for ionic conduction. They found that the majority of these gels have ionic conductivity about $10^{-3}Scm^{-1}$ even at -20^0C.**[8].**

E.Quataroneet.al. studied the long-term stability of the polymer gel electrolyte having general formula PMMA/EC/DMC/LiN(CF_3SO_2)$_2$for different ratios EC/DMC. PMMA-based gel electrolytes have shown electrical conductivity at room temperature as high as 10^{-3} Scm^{-1}.**[9].**

J. Y. Song *et.al.* described the advantages and characteristics of various polymer electrolytes in solid-state lithium-ion batteries. Plasticized or gelled electrolytes are major polymeric electrolyte materials can be used for solid-state lithium and lithium-ion batteries applications **[10].**

Xinping Hou and Kok Siong Siow have prepared a new plasticized polymer electrolyte by taking acrylonitrile-butadiene-styrene (ABS), PMMA and EC-PC as plasticizers, and $LiClO_4$ as salt. Plasticized dual-phase polymer electrolytes possess good mechanical strength and high ionic conductivity was obtained by controlling the blend ratio of ABS and PMMA, the plasticizer and $LiClO_4$ content **[11].**

J.Vondrak*et. al.* Prepared new polymer gels (based on PMMA:PC) taking Li, Na, Mg, and Zn perchlorates as salt. The conductivity of gels containing cations of smaller ionic radii (Li and Mg) is lower than that of the others **[12].**

J.Adebahr*et.al.*investigated about solvent and ion dynamics in PMMA based gels as a function of the loading of nanosized TiO2 particles. The gels were prepared with the molar ratio of 46.5:19:4.5:30 form EC, PC, lithium perchlorate and PMMA respectively. The diffusion coefficients of the lithium ions and two solvents (EC and PC) were investigated by NMR. It was shown that the addition of filler to the gel electrolytes enhances the diffusion of the cations, while the diffusion of the solvents remains constant **[13].**

G.Girish Kumar and S.Sampath prepared a gel polymer electrolyte (GPE) film comprising poly(methyl methacrylate), ethylene carbonate (EC), propylene carbonate (PC) and Zinctriflate (ZnTr) and characterized by electrochemical and spectroscopic techniques. They found the ambient temperature ionic conductivity to be 1.67×10^{-3} S cm^{-1}, along with electrochemical stability window up-to 5 V **[14].**

Upadhyaya *et. al.* prepared PMMA based Na+ ion conducting gel electrolytes. They have taken the mixture of PMMA+ PC and PMMA+(EC+ PC) in different ratio and also different

concentrations of $NaClO_4$. They observed the maximum ionic conductivity 10^{-3} S cm^{-1} at temperature 25°C **[15].**

A. Manuel Stephan reviewed the electrochemical and physical properties of various polymer gel electrolytes based on PEO, PAN, PMMA, PVC and PVdF-HFP for lithium batteries **[2].**

H.Yang *et.al.*prepared a polymer gel electrolyte (PMMA-EC/PC/DMC-NAI/I_2) and found the ionic conductivity 6.89mScm^{-1} using poly(methyl methacrylate) as polymer host, ethylene carbonate, 1,2-propanediol carbonate and dimethyle carbonate as organic mixture solvent **[16].**

M.Z.Kufian*et.al.* prepared PMMA–LiBOB gel electrolyte using PMMA, EC, PC and LiBOB as precursors. They have been concluded that conductivity of liquid electrolyte dropped on addition of PMMA from 4.8 mS cm^{-1} to 0.25 mS cm^{-1}**[17].**

N.H.Idris et al. In 2012 prepared a micro porous polymer gel electrolyte for lithium ion battery application using poly(vinylidene fluoride)/poly(methyl methacrylate) (PVDF/PMMA) using the phase-separation method. They found the maximum ionic conductivity of the polymer electrolyte at room temperature to be 1.21×10^{-3} S cm^{-1}andthe lowest activation energy to be 16.68 kJ mol^{-1}**[6].**

1.7 Objective

The main objectives of this project work are given below

- Preparation of a series of PMMA based polymer gel electrolyte by taking different ratio of O/Na ratio by gelation method.
- Studies of structural and micro structural properties using X-ray diffraction and Optical microscopic techniques.
- Studies of the change in the vibrational mode by FTIR spectroscopic techniques.
- Studies of the detailed electrical properties using complex impedance spectroscopy and dielectric spectroscopic techniques.

CHAPTER-2

SAMPLE SYNTHESIS

2.1 Synthesis of polymer gel electrolyte

There are different types of method for synthesis of polymer electrolytes such as solution cast method, hot press technique and gelation method.

1. **Solution cast method**

For preparation of polymer electrolyte, solution cast method is the easiest process. In this method desired amount of salt and polymer are dissolved in a polar solvent. After this the solution is stirred by a magnetic stirrer for the complexation of the polymer and salt. The solution formed is poured into a petridish for evaporation of the solvent giving rise to polymer electrolyte **[20].**

2. **Hot press technique**

Compared to solution cast method, hot press technique is a very fast method. It is also dry process for preparation of polymer electrolytes. The powder form of polymer and salt are taken and mixed in appropriate ratio using agate and mortar. Then the mixture is heated around the melting point of the host polymer. Result of this, a soft lump is formed which is pressed between two cold metal blocks for characterization. It forms a stable polymer electrolyte **[21].**

3. **Gelation method:-**

In this method, first appropriate amount of salt will be added in the polar solvent and mixed thoroughly by stirring till the salt will be completely dissolved. Then the polymer is added to it and the whole solution is stirred for sometimes and poured in a petridish. The solution was left for some hours for gelation. We have prepared the samples by gelation method **[22].**

2.2 Materials used for gel preparation

1.Poly(methyl methacrylate) (PMMA)

In 1985, it was found that poly(methyl methacrylate) could be used as gelating agent. It is a transparent thermoplastic polymer. PMMA is an organic glass at room temperature; i.e., its Tg is below room temperature. For synthesis of polymer gel electrolyte we have taken Poly(methyl methacrylate) (PMMA) as polymer. It could be used as gelating agent. It gives better stability to the polymer gel electrolyte. Molecular weight of PMMA varies. The chemical structure of PMMA is:

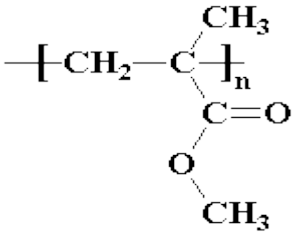


Fig: 1 chemical structure of PMMA

2. Ethylene carbonate (EC)

We have chosen Ethylene carbonate (EC) as solvent. Molecular weight of EC is 88.06g/mol. Melting point and boiling point of EC are (34-37)°C and 260.7°C respectively. The chemical structure of EC is:

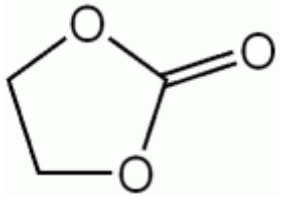


Fig: 2 chemical structure of EC

3. Propylene carbonate (PC)

Propylene carbonate (PC) is also taken as another solvent. Molecular weight of PC is 102.09g/mol. Melting point and boiling point of PC are -48.8°C and 242°C respectively. The chemical structure is:

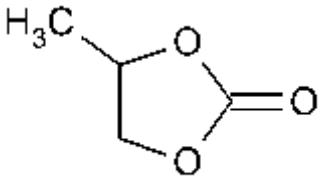


Fig: 3 chemical structure of PC

4. Sodium iodide (NaI)

Sodium iodide is taken as salt for preparation of polymer gel electrolyte. It has low lattice energy so it can easily dissociate into ion. Its molecular weight is 149.89 g/mol.

2.3 Procedure

Appropriate amount of Ethylene carbonate (EC) +Propylene carbonate (PC) (EC: PC is 1:1) were taken in a beaker and then mixed thoroughly by a glass rod. After this sodium iodide (NaI) was weighted and mixed with the EC+PC solution for the ratio of O/Na= 20, 40, 60, 80, and 100. It was again stirred by a glass rod to get a clear solution. Then appropriate amount of poly(methyl methacrylate) (PMMA) was added to the already prepared solution and stirred for sometimes for the formation of uniform mixture of the solvent and the polymer. The polymer and the solvent were taken in 2:3 ratios in the present studies. The mixtures were then poured in different petridishes and left for the formation of Gel.

Flow Chart:

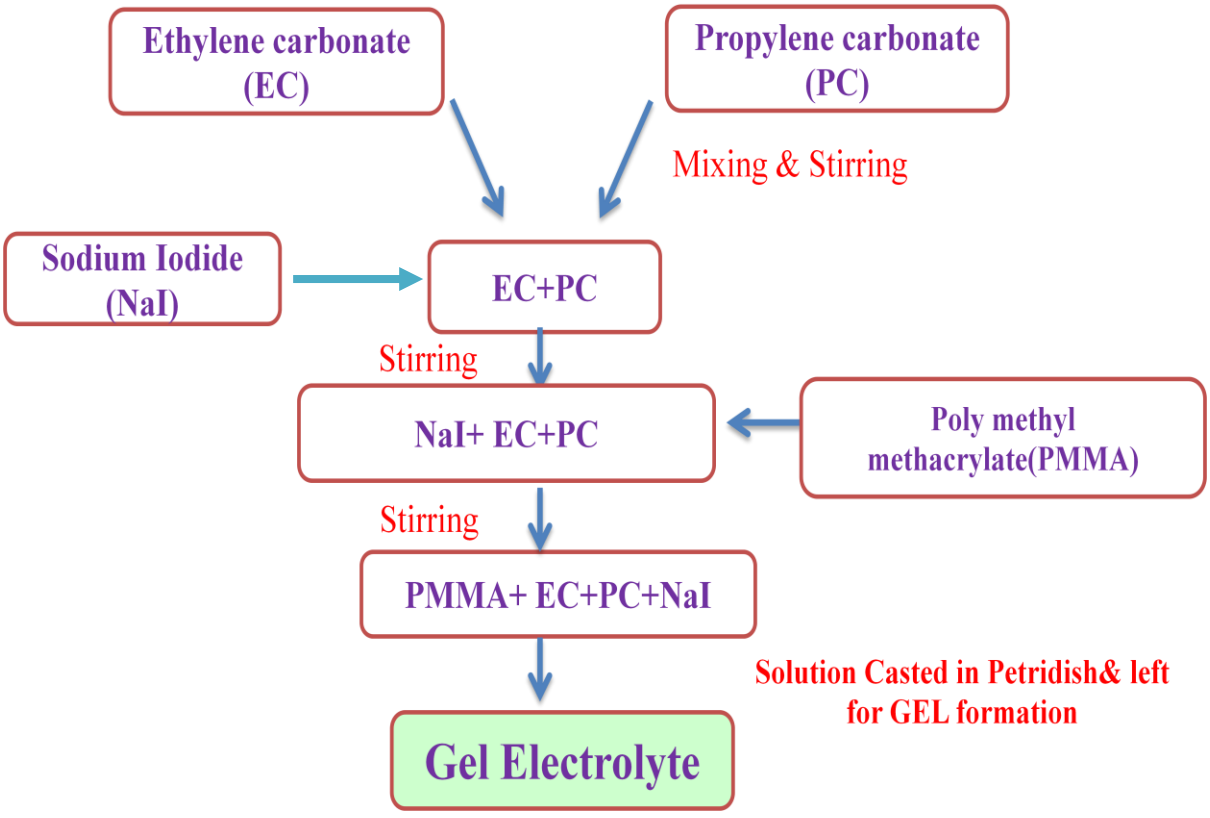


Fig: 4 Flow chart of sample preparation

CHAPTER-3

CHARCTERIZATION TECHNIQUES

3.1 X-ray diffraction

X-ray scattering techniques gives information about the crystal structure, interplanar spacing, chemical composition, interchain-separation and physical properties of materials and thin films. Bragg's law was used to explain the interference pattern of X-rays scattered by crystals. The interaction of the incident rays with the sample produces constructive interference when conditions satisfy Bragg's law i.e. $n\lambda=2d \sin\theta$ **[23].**

3.2 Optical microscopic studies

Optical microscopes are often referred as light microscope. It is a type of microscope which uses visible light and a system of lenses to magnify images of the small sample. To study the surface morphology of the sample we have used optical microscopy. In this study we have used optical microscope to observe the spherulites and the boundary between the spherulites in the polymer gel electrolyte **[19, 24].**

3.3 FTIR-Spectroscopy

In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption/transmission, creating a molecular finger print of the sample. FTIR Spectroscopy can be sued to (1) identify chain structure and physical aspects (i.e., chain orientation, crystallinity, and chain conformation or chain dynamics) of polymer electrolyte (2) determine the quality or consistency of a sample **[25].**

3.4 Dielectric spectroscopy

To study the electrical properties of the prepared gel samples we have chosen the dielectric spectroscopy technique. It is based on the interaction of an external field with the electric dipole moment of the sample and represented by permittivity values of the sample. It is the measurement of relaxation phenomena that are related to the presence of dipoles in samples i.e. it measures the dielectric properties of a medium as a function of frequency. It also measures the impedance of a system over a wide range of frequencies. Dielectric studies also give a.c. conduction variation with frequency, bulk resistance of the sample under observation **[26].**

CHAPTER-4

RESULTS AND DISCUSSIONS

4.1 X-ray Diffraction

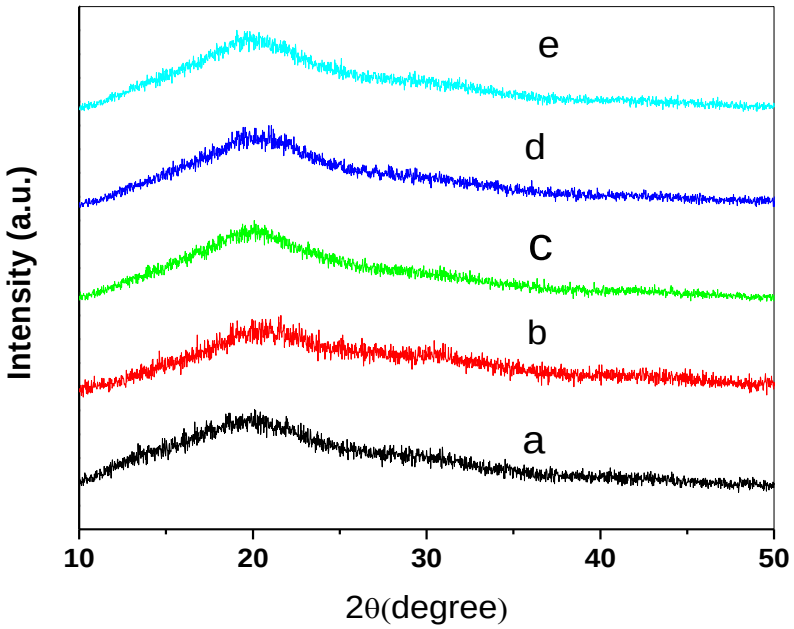


Figure: 5XRD patterns of gel electrolyte for different ratio of O/Na: (a) O/Na=20, (b) O/Na=40, (c) O/Na=60, (d) O/Na=80 and (e) O/Na=100

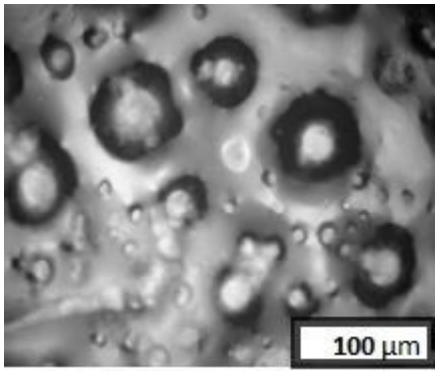
The XRD patterns of the polymer gel electrolytes were recorded at room temperature using a X-ray powder diffractometer (Philips X-ray diffractometer) with Cu kα radiation (λ = 1.5405 Å) in a wide 2θ (Bragg angle) range ($10 \leq 2\theta \leq 50$) at a scanning rate of 3 degree/min.Fig: 1 shows the XRD patterns of PMMA-based polymer gel electrolytes for different composition of O/Na: 20, 40, 60, 80 and 100. The patterns are characterized by appearance of broad peak in the lower 2θ value, suggesting the semi crystalline nature of the samples i.e., presence of both crystalline and amorphous contents. We observed the peak near 20º for all concentration of the polymer electrolytes. So we concluded that the polymer gel electrolytes are semi crystalline in nature. We can also calculate interplaner spacing and interchain separation using the formula given below:

$$R = \frac{7}{2\pi} \times \frac{\lambda}{2 \sin \theta}$$

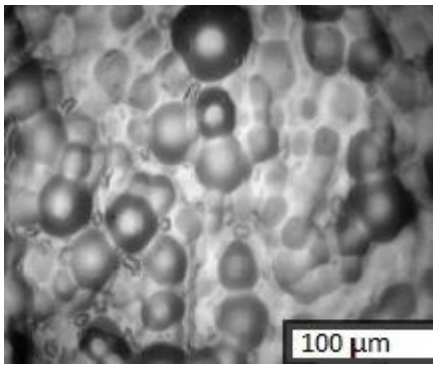
Table: 1 Calculation of inter-chain separation and interplaner spacing for different O/Na ratio of polymer gel electrolytes

O/Na	2θ (in degree)	θ (in degree)	Interchain separation d (Aº)	Interplanar spacing R (Aº)
20	20.48	10.24	4.334	4.830
40	20.34	10.17	4.362	4.862
60	20.1	10.05	4.414	4.920
80	19.9	9.95	4.460	4.971
100	19.68	9.84	4.508	5.024

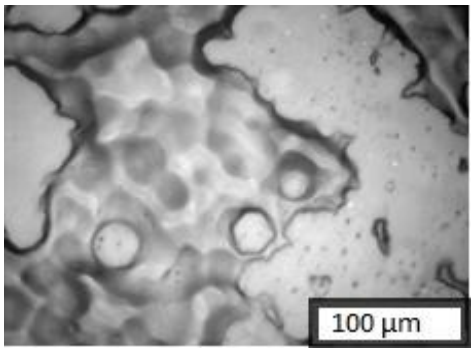
4.2 Optical microscopy



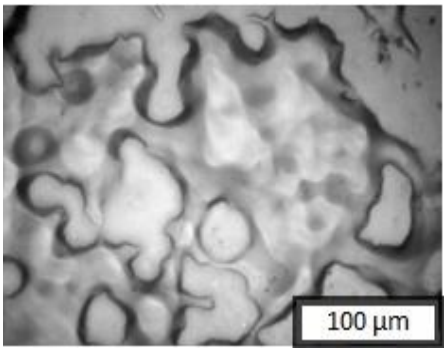
(a) Microscopic image of O/Na: 20



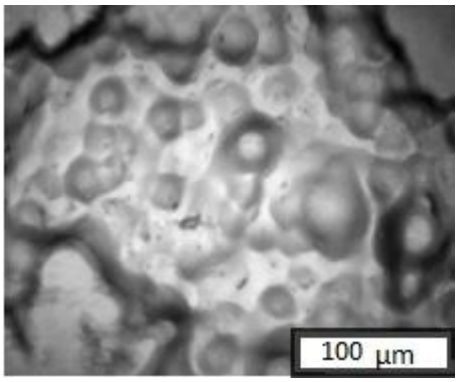
(b) Microscopic image of O/Na: 40



(c) Microscopic image of O/Na: 60



(d) Microscopic image of O/Na: 80



(e) Microscopic image of O/Na: 100

Figure: 6 Optical Microscopic image of (a)O/Na=20, (b)O/Na=40, (c)O/Na=60, (d)O/Na=80 and (e)O/Na=100

We have captured Microscopic image ofvarious O/Na ratios at different magnifications using OlympusBX51Optical Microscope at room temperature. The presences of spherulites are clearly visible for all compositions and the spherulites are separated by the boundary. The spherulite in the micrograph represents the crystalline nature and the boundary between them represents the amorphous nature. This indicates the semi crystalline nature of the samples. Thesizes of the spherulites ranges between 5-20 μm.Image of O/Na =40 is the best as far as clarity is concerned.

4.3 FTIR-Spectroscopy

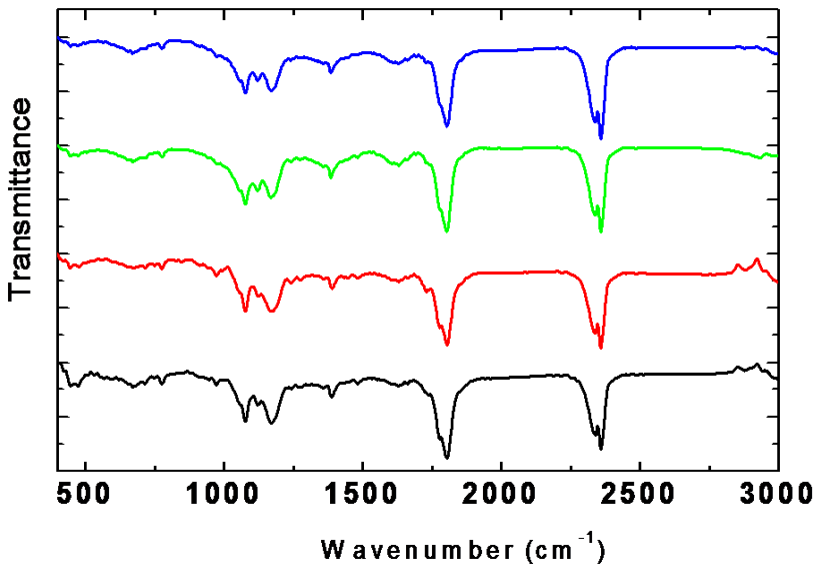


Fig: 7 FTIR spectra for different composition of O/Na

Fourier transform infrared (FTIR) spectra of the electrolytes were recorded with a FTIR spectrometer (Thermo Nicolet Corporation, NEXUS –870) from 4000 to 400 cm^{-1} with a resolution of 2 cm^{-1} at room temperature. Using FTIR spectroscopy,we can determine the chain conformation or chain dynamics about the polymer.Different types of vibrational bands are found in a particular portion of the infrared region.After the band assignment it is clear that all the absorption bands are nearly identical, and the positions are also unaffected with different salt ratios. Hence we can conclude that the polymer is not participating in any complex formation in polymer gel electrolyte, but it gives the mechanical strength to the electrolyte.

Table: 2 assignments of vibrational bands for different wave number in the FTIR spectra

Wave number(cm^{-1})	Band assigned
1168	C-O
1388	C-C
1630	C=O
1808	C=C
2360	Atmospheric Co_2 present in the sample

4.4Dielectric spectroscopy:

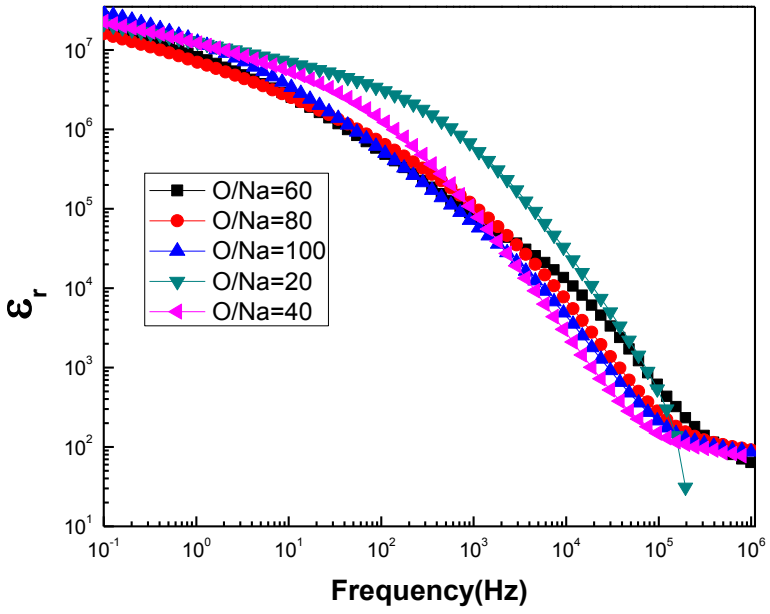


Fig: 8 Variation of dielectric constant with frequency at different ratio of O/Na.

The electrical parameters (impedance, phase, parallel capacitance and tan d)were measured using a computer-controlled impedance analyser (PSM 1735 Impedance Analysis Package (Newton 4th Ltd.)) in the frequency range of 100 mHz to 1MHz at a a.c. signal level of 100 mV at room temperatures. The polymer electrolyte film is sandwiched between two stainless steel blocking electrodes for the electrical measurement. The complex impedance spectrum data was used to evaluate the bulk d.c. Conductivity and other related electrical properties.

Fig: 8shows the variation of relative permittivity (ε_r) with frequency for different ratio of **O/Na: 20, 60, 80, and 100**at room temperature. Here the value of ε_r iscalculated using the formula $\varepsilon_r = C/C_0$, where C_p is denoted as capacitance of a parallel plate capacitor and c_0 is the geometrical capacitance considering vacuum with in the capacitor plates. $C_0$is calculated using the formula $\varepsilon_0 A/d$ where A and d are the area and thickness of the sample. At lower frequencies, permittivity (ε_r) has higher value but it decreases with increase in frequency. The decrease in the value of ε_r with increase of frequency is due to relaxation processes. The higher value of dielectric constant at low frequency regions indicates the presence of electrode polarization phenomena.

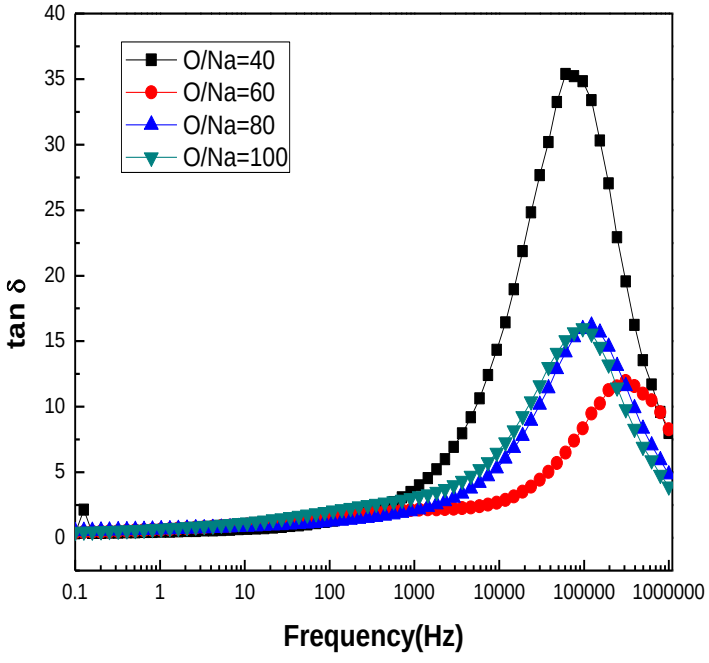


Fig: 9 tangent loss verses frequency of gel electrolytes at different ratio of O/Na

Fig: 9 shows the variation of tangent loss with frequency for the ratio of **O/Na: 40, 60, 80, and 100.** We found that when frequency increases tangent loss value increases, at certain value of the frequency the value of tangent loss is maximum which is shown by a peak and then tangent loss value decreases with increase of frequency. The appearance of peaks suggests the presence of relaxing dipoles in the samples.

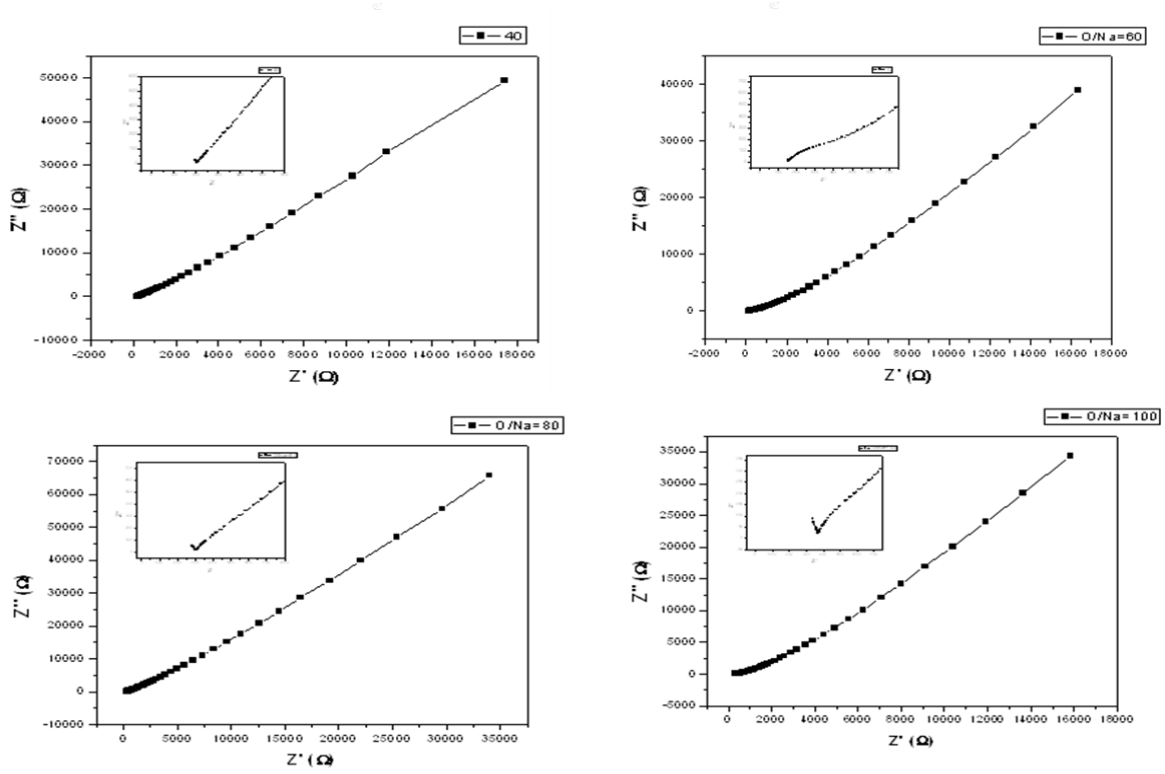


Fig:10 Z" verses Z' for different ratio of O/Na

Fig: 10 show the variation of Z" with Z' for different concentration of O/Na. In all the figures, there is a semi-circular arc (due to lack of experimental points, it is not clearly visible)in the high frequency region suggesting the bulk properties of the material and a spike in the low frequency region. We can calculate bulk resistance from the intercept of the semi-circular arc and by taking the value of bulk resistance we can calculate the d.c. conductivity. The formula used for the calculation of d.c. conductivity is given by

$$\sigma_{dc} = \frac{1}{R_b} \times \frac{l}{A}$$

Here R_b is the bulk resistance and A is the area and l is the thickness of the sample.

Table: 3 Calculation of D.C. conductivity (σ_{dc}) for different composition of O/Na

O/Na	σ_{dc}
40	2.86×10^{-4}
60	3.06×10^{-4}
80	2.37×10^{-4}
100	1.83×10^{-4}

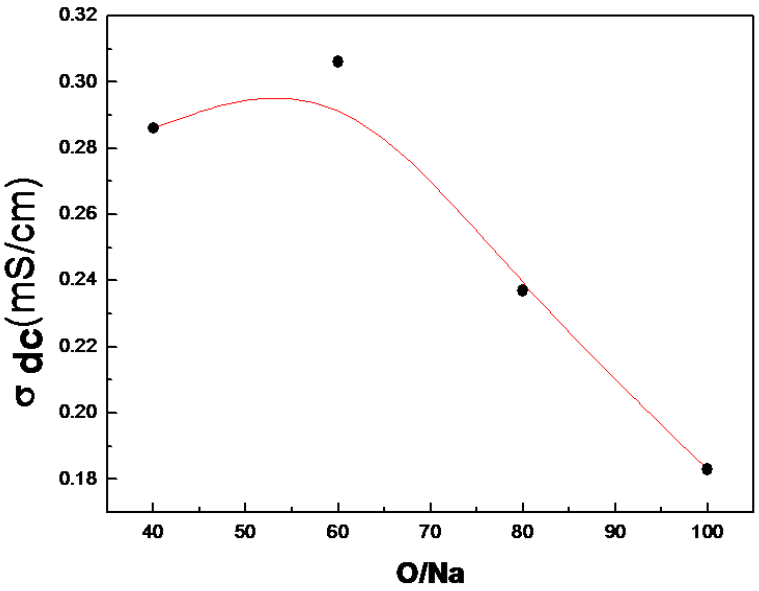


Fig: 11 variation of d.c. conductivity with O/Na ratio.

Fig: 11 shows the variation of d.c. conductivity with O/Na ratio. From the figure it has been observed thatd.c. conductivity increases with increase in O/Na ratio than attains a maximum and then gradually starts decreasing. As we can see that maximum d.c. conductivity is at O/Na=60.

CHAPTER-5

CONCLUSION

Polymer gel electrolytes were prepared for different composition of O/Na (i.e. 20, 40, 60, 80 and 100) by gelation method, taking PMMA as polymer, EC-PC as solvent and NaI as salt. The prepared samples are characterized using different experimental techniques. For structural, morphological and vibrational properties we used X-ray diffraction and optical microscopy and FTIR spectroscopy. Complex impedance spectroscopic technique has been adopted to study the electrical properties of the electrolytes. The following conclusions were drawn from the studies:

- X-ray diffraction technique indicates the semi crystalline nature of the prepared sample.
- From the optical microscopy images, the spherulites are clearly visible and their size ranges from 5-20 micro meters. The nature of the spherulites indicated that the prepared samples are semi crystalline.
- As the FTIR spectra are same for different composition of O/Na, we concluded that the polymer is not participating in any complexation process for polymer gel electrolyte.
- Dielectric Spectroscopy was carried out to analyse the dielectric and electrical behaviour of polymer gel electrolyte. The appearance of dielectric loss peak in dielectric loss versus frequency plot indicates that the relaxation is dipolar in nature.
- The d. c. conductivity of the materials was calculated from complex impedance plots. From d.c. conductivity graph, the maximum value of conductivity is found to be 3.06×10^{-4} S/cm for O/Na=60 at room temperature.

REFERENCES

[1] S. Glasstone: *An introduction to electrochemistry*; (11)1974

[2] A.Manual Stephan: *European polymer journal*; **42**(21-42)2006

[3] S.Chandra: *Superionic solids (Principle and application)*; 1981

[4] R.C.Agarwal et.al: *Journal of material science*; **34**(1131-1162)1999

[5] S.Chandra et.al: proc. Natl. Acad. Science; **64**(141)1994

[6] N.H.Idris, Md. M.Rahaman, Jia-Z Wang and Hua-Kun Liu: *Journal of power supply*; **201**(294-300)2012

[7]O. Bohnke, C. Rousselot, P.A. Gillet, C. Truche, *Journal of Electrochemical*;**139**(1862) 1992

[8] A.M.Voiceet. al: *Polymer papers*; **35**(3363-3372)1994

[9] E.Quatarone, C.Tomasi, P.Mustarelli, G.B.appetecchi and F.Croce: Physical chemistry; **43**(1435-1439)1998

[10]J.Y. Song, Y.Y. Wang, C.C. Wan, Journal *of Power Sources*;**77**(183–197) 1999

[11] XinpingHou and Kok-SiongSiow: *Journal of polymer*; **41**(8689-8696)2000

[12] JirVondrak , Marie Sedlarkova, Jana Velicka , BretislavKlapste, Vtezslav Novak , Jakub Reiter, *Electro Chemical acta*; **46**(2047-2048)2001

[13] J.Adebahr et.al: *Electro chemical Acta*; **48**(2099-2103)2003

[14] G.Girish Kumar and S.Sampath: *Solid state Ionic*; **176**(773-780)2005

[15]H.M. Upadhaya, R.K. Yadav, A.K. Thakur, S.A. Hasmi: *Ion conducting materials* (2001)

[16] H.Yanget. al: *material chemistry and physics*; **110**(38-42)2008

[17]M.Z.Kufian et.al: *Solid state Ionics*; **208**(36-42)2012

[18]C. Svanberg , W. Pyckhout-Hintzen , L. B¨orjesson; *ElectrochimicaActa*;**51** (4153–4156)2006

[19] Philip D. Rack: *Optical Microscopy*; University of Tennessee, Dept. of Materials Science and Engineering

[20] R C Agrawaland G P Pandey: *Journal of physics D: Applied physics*;

41 (223001)2008

[21] T. Michot et al.: *ElectrochimicaActa*;**45** (1347–1360)2000

[22] S. Murai et al.: *Journal of Photochemistry and Photobiology A: Chemistry*; **148** (33–39) 2002

[23] www.scintag.com,*Basic of x-ray diffraction*

[24] Davidson and Abramowitz: *Optical Microscopy*; National High Magnetic Field Laboratory, The Florida State University

[25] Donald L Pavla, Gary M. Lampman, George S. Krlz, James R. Vyvyan; *Introduction to spectroscopy*; Department of Chemistry

[26] Charles Kittel: *Introduction to solid state physics*; 7th ED